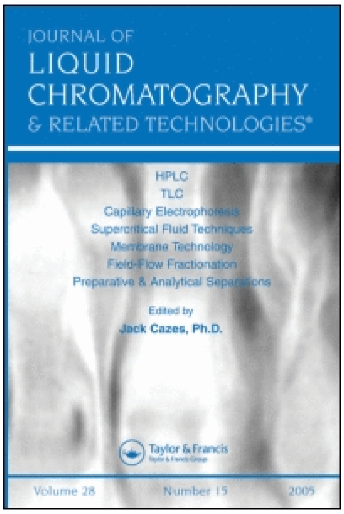

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Mohamed E. Mahmoud[a]
[a] Faculty of Medicine and Allied Sciences, Medical Chemistry Department, King Abullaziz University, Jeddah, Kingdom of Saudi Arabia

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STUDY OF THE SELECTIVITY CHARACTERISTICS INCORPORATED INTO PHYSICALLY ADSORBED ALUMINA PHASES. II. MERCAPTONICOTINIC ACID AND POTENTIAL APPLICATIONS AS SELECTIVE STATIONARY PHASES FOR SEPARATION, EXTRACTION, AND PRECONCENTRATION OF LEAD(II) AND COPPER(II)

Mohamed E. Mahmoud

Faculty of Medicine and Allied Sciences, Medical
Chemistry Department, King Abullaziz University,
P.O. Box 80205, Jeddah 21589, Kingdom of Saudi Arabia

ABSTRACT

A method is described for the immobilization of 2-mercaptonicotinic acid on the surface of three different alumina phases. The selected alumina phases are characterized by different acidity properties, acidic phase (I), neutral phase (II), and basic phase (III). Evidences for the physical adsorption of the organic modifier on the surface of the newly synthesized alumina phases (IV–VI) were evaluated on the basis of infrared spectrophotometric analysis, as well as the surface coverage values and pH values of all alumina phases (I–VI). The determined mmol g^{-1} values for the modified alumina were found to be 0.886, 1.012, and 0.958 for the modified acidic phase (IV), neutral phase (V), and basic phase (VI), respectively.

These alumina phases (I–VI) were extensively investigated to identify the possible selectivity characters incorporated into the modified alumina phases and compared with the unmodified ones. This study was accomplished by the determination of the distribution coefficient value (K_d), as well as the separation factor (α) for a series of mono-, di-, and trivalent metal ions.

The results of this study were found to confirm the strong affinity and selectivity of the modified alumina phases (IV–VI) for Pb(II) and Cu(II), due to the noticeably high increase in their separation factors versus other interfering metal ions. The advantage of the selectivity character in the modified phases (IV–VI) was also confirmed by the application of a micro-column for selective separation of Cu(II) and Pb(II) from other interfering metal ions, such as Ca(II), Cr(III), Co(II), and Cd(II). Finally, a micro-column was also used and applied for the selective separation, extraction, and preconcentration of Cu(II) and Pb(II) from sea water samples, and the results indicated good recovery values for the spiked $1.0\,\mathrm{ng\,mL^{-1}}$ of these two metal ions. The percentage recovery values of Cu(II) and Pb(II) were found to be in the range of $95.2–98.7 \pm 2.0–4.0\%$ by the three physically adsorbed alumina phases with 2-mercaptonicotinic acid (IV–VI), with a preconcentration factor of 500.

INTRODUCTION

Synthesis of new stationary phases for chromatographic applications, as well as solid phase extraction technique, is mainly based on the process of immobilization of organic compounds on the surface of inorganic or organic solid supports.[1] The modified inorganic solid sorbent, silica gel as an example, is commonly used in liquid chromatography, as well as high performance liquid chromatography.[2–4] Gas chromatography was also used for application of the modified solid supports as stationary phases.[5,6] Other chromatographic techniques, such as high performance thin layer (HPTLC),[7] capillary electrochromatography (CEC),[8] size exclusion chromatography (SEC),[9] and super critical fluid chromatography (SCF)[10] were also found to utilize modified stationary phases based on silica gel matrix. Other modified inorganic solid sorbents as zeolite and volcanic tuff were found to exhibit good chromatographic behavior in thin layer chromatography.[11]

On the other hand, modified solid supports such as silica gel, especially those synthesized by loading chelating compounds, were recently proven to show good affinity and selectivity characters for binding, extraction, removal, and preconcentration of various metal ions from different matrices by micro-column separation via interfacing with on-line or off-line detection methods of analysis, such as AAS, ICP, or ICP-MS.[12–22]

Alumina is considered the second most commonly used inorganic solid support, with its major applications focused on the study of adsorption behaviors and mechanisms of organic and inorganic species.[23–25] Adsorption and immobilization of chelating compounds on the surface of alumina for their uses and applications in chromatography and normal or selective solid phase extraction and preconcentration of various metal ions are limited.[26] The presence of alumina phases in three different forms, mainly acidic, neutral, and basic types, can afford a wide range of sorbents for applications in different disciplines. In a recent report, basic alumina and silica gel were physically adsorbed with 2-hydroxy-2-mercaptopyrimidine (2-thiouracil), and the modified alumina phase was found to be highly selective for separation and extraction of cadmium (II) from natural water samples.[27] This trend has prompted us to study and evaluate the adsorption of 2-mercaptonicotinic acid, as a good chelating compound, on the surface of three different alumina phases, acidic, neutral, and basic types, as well as the utilization of these newly modified alumina phases in micro-column separation, extraction, and preconcentration of various tested metal ions, with a strong emphasis on the possible variations in the selectivity incorporated into these modified alumina phases.

EXPERIMENTAL

Reagents and Materials

Three alumina types of standard grade (150 mesh, 58 Å and surface area = 155 m^2/g) were purchased from Aldrich Chemical, USA. The first type is an acidic alumina (I) with a pH value of aqueous suspension = 4.5 ± 0.5. The second is a neutral alumina phase (II) with a pH value of aqueous suspension of 7.0 ± 0.5, and the third alumina is a basic type (III) with a pH value of 9.5 ± 0.5. The metal salts are all of analytical grade and purchased from BDH Chemical, Poole, UK. 2-mercaptonicotinic acid was purchased from Aldrich Chemical, USA and used as received. For preparation of metal solutions, double distilled water (DDW) was used.

Synthesis of Alumina—Physically Adsorbed 2-Mercaptonicotinic Acid Phases (IV–VI)

2-Mercaptonicotinic acid (9.30 g, 30 mmol) was dissolved in 750 mL ethanol, and to this solution 10.0 g of either alumina phase (I), (II), or (III) was then added. The reaction mixture was heated under reflux for 6 h. The modified acidic alumina (IV), neutral alumina (V), or basic alumina (VI) was filtered, washed with ethanol and diethylether, and dried in an oven at 70°C for 5 h.

Determination of the Surface Coverage Values by Thermal Desorption Method

100 mg of the modified or unmodified alumina phases (I–VI) was weighed in a dry porcelain crucible and this was gradually heated into a furnace from 50°C to 500°C. The ignition was completed in 1 h and the remaining alumina phase was left to cool in a desiccator and weighed to determine the mass of desorbed organic compound.

Determination of the Distribution Coefficient (k_d) Values for Various Metal Ions by Alumina Phases (I–VI)

A series of mono-, di-, and trivalent metal ions, viz. Na(I), K(I), Mg(II), Ca(II), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) was selected to conduct this study. 1.0 $\mu g\, mL^{-1}$ solution of each metal ion was prepared in DDW. 100 mg of the selected alumina phase was weighed in a 100 mL measuring flask. 50 mL of the metal ion solution was then added and the reaction mixture was automatically shaken for 2 h. The mixture was then filtered and 1.0 mL of concentrated nitric acid was added to the eluent. Standard and blank solutions were also prepared in a similar way.

Selective Separation of Metal Ions by a Micro-Column Packed with Alumina Phases (I–VI)

A micro-column[18,19] was prepared by packing 250 mg of alumina phases (I–VI). A solution of the metal ions was prepared from 1.0 $\mu g\, mL^{-1}$ of Ca(II), Cr(III), Cu(II), Cd(II), and Pb(II). 1000 mL of this solution was passed over this micro-column with a flow rate of 10.0 $mL\, min^{-1}$. The desorbed metal ions in the eluent were directly determined by flame atomic absorption analysis (AAS). The adsorbed metal ions on the surface of alumina phase was then desorbed by the passage of 2.0 mL concentrated nitric acid. The concentration of the preconcentrated metal ions was also determined by AAS.

Selective Extraction and Preconcentration of Pb(II) and Cu(II) from Artificial Sea Water Samples by a Micro-Column

A one liter sample of artificial sea water was spiked with 1.0 ng mL^{-1} Pb(II) or Cu(II). This solution was passed over a micro-column packed with 100 mg of the selected modified alumina phases (IV–VI) with a flow rate of 10.0 mL min^{-1}. The adsorbed metal ions on the surface of alumina phase was eluted with 2.0 mL concentrated nitric acid and determined by AAS.

Apparatus

Infrared spectra of the modified and unmodified alumina phases (I–VI) were carried out from KBr by a Perkin–Elmer 1430 ratio recording spectrophotometer. Surface coverage determination by the thermal desorption method was done by a Thermolyn 47900 furnace. The pH measurements of the modified and unmodified alumina phases (I–VI) were conducted by an Orion EA 920 pH-meter, which is calibrated against two standard buffer solutions of pH 4.0 and 9.2. Atomic absorption analysis of Na(I) and K(I) were performed by a flame photometric analysis with a Corning clinical flame photometric 410°C. The other metal ions were determined by a Perkin–Elmer 2380 flame atopmic absorption spectrophotometer.

RESULTS AND DISCUSSION

Surface Coverage and Modification of Alumina Surface

The surface modification of solid sorbents, such as alumina or silica with organic modifier, can be mainly interpreted on the basis of infrared spectrophotometric analysis, as well as the determination of surface coverage values.[1] The infrared spectra of the unmodified alumina phases (I–III) are characterized by the presence of three major infrared peaks at 3600–3400, 1650, and 1000–400 cm^{-1}, which are mainly due to the alumina matrix.[23] However, immobilization of 2-mercaptonicotinic acid on the surface of these three alumina phases to produce the three modified alumina phases (IV–VI) were found to exhibit several characteristic peaks that are centered at 3019–3028, 2590–2595, and 1739–1750 cm^{-1}, and account for the presence $\nu_{=C-H}$, ν_{S-H}, and $\nu_{C=O}$, respectively.[29]

Table 1. Surface Coverage and Modification of Alumina Phases with 2-Mercaptonicotinic Acid

Alumina Phase	PH	Surface Coverage (mmol g^{-1})	Major Infrared Peaks (cm^{-1})
(I)	4.4	–	3600–3400, 1650, 1000–400
(II)	6.6	–	3600–3400, 1650, 1000–400
(III)	8.9	–	3600–3400, 1650, 1000–400
(IV)	3.4	0.886	3019, 2595, 1745
(V)	3.7	1.012	3025, 2590, 1739
(VI)	4.2	0.958	3028, 2593, 1750

The surface coverage of the modified alumina phases (IV–VI) can be determined by several well-known methods, such as the metal probe testing method,[30] and carbon and nitrogen contents analysis,[31] as well as the thermal desorption method.[23] The values of mmol g^{-1} of surface coverage listed in Table 1 are determined on the basis of the thermal desorption method and found to correspond to 0.886, 1.012, and 0.958 for alumina phases (IV), (V), and (VI), respectively. These values, along with the infrared data, clearly refer to the good adsorption behavior of 2-mercaptonicotinic acid on the surface of acidic, neutral, and basic alumina types.

Table 1 also compiles the pH values of the modified and unmodified alumina phases (I–VI) for the sake of comparison. It is evident from these data that the adsorption of the organic modifier, 2-mercaptonicotinic acid, has led to high changes in the acidic properties of the unmodified alumina phases (I–III). The final pH values of the modified alumina phases (IV–VI) are very close and range in pH 3.4–4.2 due to the acidic properties of the organic modifier.

The Distribution Coefficient (K_d) and Separation Factor (α) of Various Metal Ions by Alumina Phases (I–VI)

The distribution coefficient values[13] for the unmodified alumina phases (I–III), as well as the physically adsorbed alumina phases by 2–mercaptonicotinic acid (IV–VI) are given in Table 2. It evident from the listed data that basic alumina phase (III) is the most superior one in the process of metal ion extraction from aqueous solutions compared to the two other acidic and neutral alumina phases (I) and (II), respectively. Most of the K_d-values of the tested metal ions were found to increase from acidic to neutral to basic alumina phases. The highest extracted metal ions by these three unmodified alumina phases are Pb(II), Cd(II), Cu(II), Zn(II), and Cr(III). The other tested metal ions, such as Na(I), K(I), Mg(II)

Table 2. Distribution Coefficient Values (K_d) of Various Metal Ions by Alumina Phases (I–VI)

Metal Ion	Alumina (I)	Alumina (II)	Alumina (III)	Alumina (IV)	Alumina (V)	Alumina (VI)
Pb(II)	1610	11,090	25,600	470	512	3840
Cd(II)	355	2457	11,648	72	122	160
Zn(II)	369	2600	14,600	96	86	258
Cu(II)	649	3508	21,700	10,750	7020	9545
Ni(II)	366	1046	6025	215	59	201
Co(II)	247	1053	2270	57	117	123
Mn(II)	145	160	493	24	52	45
Cr(III)	869	2325	14,000	27	144	60
Ca(II)	143	154	643	23	64	41
Mg(II)	140	162	582	25	58	38
K(I)	133	141	284	21	18	26
Na(I)	125	145	259	13	15	20

Ca(II), Mn(II), and Co(II) were found to be minimally extracted by these three alumina phases (I–III).

The capability of chelating organic modifiers to strongly interact with metal ions via complex formations is mainly based on the presence of some donor atoms such as sulfur, oxygen, and nitrogen.[17,32] These donor atoms are the basic reason for incorporation of certain selectivity characters into the modified solid supports.[32] Therefore, the surface modification of the unmodified alumina phases with 2-mercaptonicotinic acid for the formation of newly synthesized alumina phases (IV–VI) was found to induce several important trends in the process of metal binding and extraction by these modified alumina phases (IV–VI). The first trend is the lower distribution coefficient values for most metal ions as compared to those determined by the unmodified alumina phases. Second, is the high selectivity characters incorporated into the newly modified alumina phases (IV–VI) for binding and extraction of Cu(II) and Pb(II). The highest distribution coefficient values by alumina phases (IV–VI) for most tested metal ions were found to correspond to alumina phase (VI), except Cu(II) which was found to be highly extracted by the modified alumina phase (IV) with a K_d value = 10750. The third trend is reported for the weak affinity of the other ten metal ions for binding and extraction by the modified alumina phases (IV–VI). These weakly bound metal ions are Na(I), K(I), Mg(II), Ca(II), Cr(III), Mn(II), Co(II), Ni(II), Zn(II), and Cd(II).

The selectivity characters incorporated into the modified alumina phases (IV–VI) via the physical adsorption of the good chelating properties of

2-mercaptonicotinic acid can be further identified and explored by calculation of the separation factor (α).[13] This value is denoted as $\alpha_{M/IM}$, where M is the analyte of interest and IM is the interfering metal ion. The calculated separation factors for the various metal ions by the modified and unmodified alumina phases (I–VI) are listed in Table 3. These values are important and essential for the evaluation of such incorporated selectivity in the modified alumina phases (IV–VI). It is also known that as the separation factor increases, the selective separation and extraction of the target metal ion from the interfering metal ion increases.

The modification of basic alumina phase (III) with 2-mercaptonicotinic acid for the formation of phase (VI) has led to a good noticeable separation efficiency of this modified phase for extraction of Pb(II) from other interfering metal ions as Cd(II), Zn(II), and Cr(III). There is an improvement in the separation factor ($\alpha_{Pb/IM}$) versus these tested metal ions from 2.2, 1.8, and 1.8 to 24, 14.9, and 64 for Cd(II), Zn(II), and Cr(III), respectively. In addition, little or no improvement in the separation factor ($\alpha_{Pb/IM}$) was evident by the modified alumina phase (V) compared to the unmodified alumina one (II). The same observation and trends can be also outlined for the separation factor of Cu(II) versus the other interfering metal ions, as listed in Table 4.

The results of the separation factor for both Pb(II) and Cu(II) versus other interfering metal ions indicate that the surface modification of acidic, neutral, and basic alumina with 2-mercaptonicotinic acid was found to produce an excellent improvement in the surface reactivity and selectivity for both Pb(II) and Cu(II)

Table 3. Separation Factor ($\alpha_{Pb/IM}$) for Lead Versus Other Interfering Metal Ions by Alumina Phases (I–VI)

Interfering Metal Ion (IM)	Alumina (I)	Alumina (II)	Alumina (III)	Alumina (IV)	Alumina (V)	Alumina (VI)
Cd(II)	**4.5**	**4.5**	**2.2**	**6.5**	**4.2**	**24.0**
Zn(II)	4.4	4.3	1.8	4.9	6.0	**14.9**
Cu(II)	2.5	3.2	1.2	–	–	–
Ni(II)	4.4	10.6	4.2	2.2	8.7	19.1
Co(II)	6.5	10.5	11.3	8.2	4.4	31.2
Mn(II)	11.1	69.3	51.9	19.6	9.8	85.3
Cr(III)	1.9	4.8	1.8	17.4	3.6	64.0
Ca(II)	11.3	72.0	39.8	20.4	8.0	93.7
Mg(II)	11.5	68.5	44.0	18.8	8.8	101.1
K(I)	12.1	78.7	90.1	22.4	28.4	147.7
Na(I)	12.9	76.5	98.8	36.2	34.1	192.0

Table 4. Separation Factor ($\alpha_{Cu/IM}$) for Copper (II) Versus Other Interfering Metal Ions by Alumina Phases (I–VI)

Interfering Metal Ion (IM)	Alumina (I)	Alumina (II)	Alumina (III)	Alumina (IV)	Alumina (V)	Alumina (VI)
Pb(II)	–	–	–	22.9	13.7	2.5
Cd(II)	1.8	1.4	1.9	149.3	57.5	59.7
Zn(II)	1.8	1.3	1.5	112.0	81.6	37.0
Ni(II)	1.8	3.4	3.6	50.0	119.0	47.5
Co(II)	2.6	3.3	9.6	188.6	60.0	77.6
Mn(II)	4.5	21.9	44.0	447.9	135.0	212.1
Cr(III)	0.7	1.5	1.6	398.1	48.8	159.1
Ca(II)	4.5	22.8	33.7	476.4	109.7	232.8
Mg(II)	4.6	21.7	37.3	430.0	121.0	251.2
K(I)	4.9	24.9	76.4	511.9	390.0	367.1
Na(I)	5.2	24.2	83.8	826.9	468.0	477.3

from any other interfering metal ion(s). This selective separation of these two metal ions by the unmodified alumina phases (I–III) are not exclusive for all tested metal ions, but only for few metal ions, especially Na(I), K(I), Mg(II), and Ca(II) with low separation factors as well.

Selective Micro-Column Separation of Metal Ions by Alumina Phases (I–VI)

The separation factors listed in Table 3 and 4 are calculated from the theoretical evaluations of the distribution coefficient values. To practically confirm the role of selectivity characters incorporated into the modified alumina phases (IV–VI) and to compare with those of the unmodified alumina phases (I–III), a full chromatographic study, based on using a micro-column separation and preconcentration of the various metal ions, was performed. The tested metal ions mixture was prepared by mixing equal concentration, $1.0\,\mu g\,mL^{-1}$ of Pb(II), Cd(II), Cu(II), Cr(III), and Ca(II). The interactions of these metal ions with the surface of the modified and unmodified alumina phases (I–VI) are represented in Figure 1. It is evident that there is high interference of the metal ions via adsorption and binding with the surface of unmodified alumina phases, especially phase (III). However, the selective sorption and binding of Cu(II) and Pb(II) by the physically adsorbed alumina phases (IV–VI) were found to be highly dominant compared to Cd(II), Cr(III), and Ca(II).

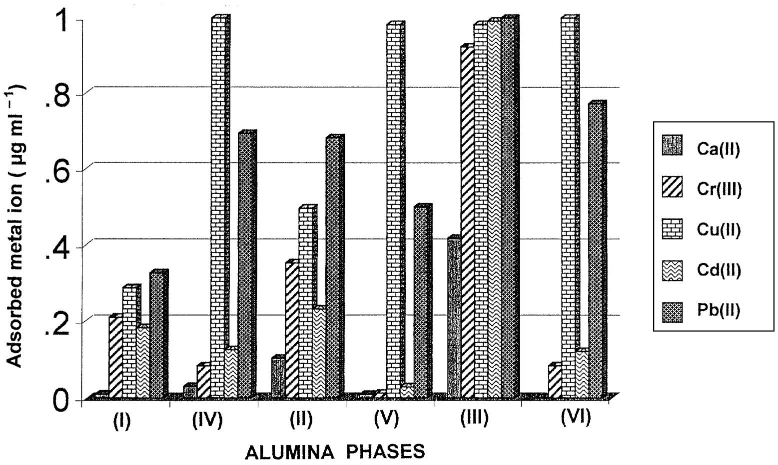

Figure 1. Selective micro-column separation of metal ions by alumina phases (I–VI).

Selective Micro-Column Separation and Preconcentration of Pb(II) and Cu(II) from Artificial Sea Water

The determination of actual concentration of trace metal ions in real samples, especially ng mL^{-1} or less, is not possible by the conventional atomic absorption spectrophotometry, due to the limitation of detection limits, as well as the matrix effects.[33,34] In order to determine such low concentration levels, a preconcentration micro-column must be used and interfaced either in the form of on-line or off-line with AAS. The packing materials in this micro-column must allow efficient and direct extraction and preconcentration of the target analyte from the bulk of matrix.

The high selectivity incorporated into the three newly synthesized alumina phases (IV–VI), based on the physical adsorption of 2-mercaptonicotinic acid, was also studied and investigated by the potential applications of these phases for separation, extraction, and preconcentration of trace concentration levels of Cu(II) and Pb(II) from artificial sea water samples. In this study, a concentration of ~1.0 ng mL^{-1} of Cu (II) or Pb(II) was spiked in one liter of artificial sea water. This solution was passed over a micro-column packed with 100 mg of the selected alumina phase (IV–VI). The preconcentrated metal ions were then determined by the off-line atomic absorption spectrophotometric analysis and the results of this study are listed in Table 5.

It is clear from the data given that excellent separation, extraction, and preconcentration procedures were accomplished, judging from the percentage recovery values of the tested metal ions. The average recovery values of Cu(II)

Table 5. Selective Adsorption of Lead(II) and Copper(II) from Artificial Sea Water Samples by Off-line Micro-column Preconcentration

Sample	(1)	(2)	(3)	(4)	(5)	(6)
Sample volume	1000 mL	1000 mL	1000 mL	1000 mL	1000 mL	1000 mL
Alumina phase	100m g (IV)	100m g (V)	100m g (VI)	100m g (IV)	100m g (V)	100 m g (VI)
Metal ion	Pb(II)	Pb(II)	Pb(II)	Cu(II)	Cu(II)	Cu(II)
Spiked metal ion (ng mL^{-1})	1.010	1.010	1.010	1.080	1.080	1.080
Preconcentration reagent	2 mL HNO_3	2 mL HNO_3	2 mL HNO_3	2 mL HNO_3	2 mL HNO_3	2 mL HNO_3
Preconcentration factor	500	500	500	500	500	500
Detected metal ion (μg mL^{-1})	0.490	0.497	0.495	0.514	0.533	0.528
Percent recovery	97.0 ± 3.0%	98.5 ± 3.0%	98.0 ± 3.0%	95.2 ± 3.0%	98.7 ± 3.0%	97.7 ± 4.0%

Percentage recovery values are base on triplicate analysis.

were found to be 95.2 ± 3.0%, 98.7 ± 3.0% and 97.7 ± 4.0% for the modified alumina phases (IV), (V), and (VI), respectively. Similar and close percentage recovery values for Pb(II) were also found as 97.0 ± 3.0%, 98.5 ± 3.0%, and 98.0 ± 3.0% by the modified alumina phases (IV), (V), and (VI), respectively, and by establishing a good preconcentration factor of 500.

These recovery values provide additional evidence for the potential application of the newly modified alumina phases (IV–VI) for selective separation of Pb(II) and Cu(II) from a sea water sample, without any interference caused by the presence of high salinity, or generally, by the matrix effects.

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